Simulation of cyclics and degradation product formation in polyethylene terephthalate reactors

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The second stage of a batch polyethylene terephthalate (PET) reactor with a kinetic scheme consisting of side reactions like thermal degradation, redistribution, cyclization and reaction with monofunctional compounds (cetyl alcohol), in addition to the major polycondensation step, has been simulated. The cyclization equilibrium has been shown by Semlyen for various cyclic compounds to be chain-length-dependent[1]. Mass balance for various side products and the polymer, PET, have been carefully worked out and the resulting set of differential equations have been solved for the molecular weight distribution (*MWD*) of the polymer. It is found that the cyclization reaction has considerable effect on the polydispersity index of the polymer even though the total quantity of cyclic compound is no more than 5%. The effect of variation of temperature and initial concentration of monofunctional compound was found to have little influence on the polydispersity index of the polymer. Since the removal of the condensation product does not become diffusion-controlled till the average chain length of the polymer reaches the value of 30, the reaction mass can be assumed to attain a uniform ethylene glycol concentration for a given applied vacuum and can be determined by the vapour–liquid equilibrium relation. The fractional level of ethylene glycol concentration, [G] ($\equiv$ [EG]/[P$_1$]$_0$), has been taken as a parameter and the *MWD* results were found to vary the redistribution rate constant with sensitivity increasing with decreasing [G]. It was shown that the importance of the redistribution reaction is increased when the cyclization reaction also occurs.

Keywords Simulation; cyclics; degradation product; polyethylene terephthalate; reactors; kinetics; thermal degradation; redistribution; cyclization

INTRODUCTION

In industrial practice[2] polyethylene terephthalate, PET, is produced in three stages. In the first step, dimethyl terephthalate, DMT, is reacted in excess of ethylene glycol to produce bis(2-hydroxyethyl terephthalate), BHET. This serves as the monomer to the second stage where it is polymerized to about 90% conversion. In the third stage, polymerization takes place in a special wiped-film reactor because the overall reaction by then becomes mass-transfer-controlled.

In this work we focus our attention on the second stage of polymerization. The main reaction in this reactor is the polymerization of BHET which is sometimes called a polycondensation reaction. There are, however, several side reactions occurring in the reaction which drastically change the nature of the polymer formed. Some of these, which have been considered in this work, are shown in *Table 1*. In our earlier studies[3-5] on the simulation of PET reactors, we showed the effect of the cyclization reaction on the molecular weight distribution (*MWD*) of the polymer formed. Even though the total amount of cyclic compounds formed was less than 5%, the change in the *MWD* was found to be considerable.

The polycondensation of BHET has been studied by several workers[6-9]. The uncatalysed reaction was studied by Challa, who carried out experiments in sealed tubes. He reported the rate and the equilibrium constants for

this step. Polyesters also undergo a redistribution reaction as shown below:
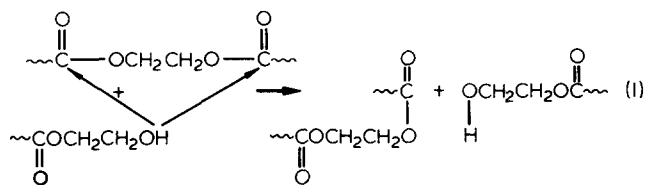
This has also been called by Flory the ester interchange reaction and Challa has measured the rate constant experimentally for this reaction. The importance of the redistribution step has been reported in recent reviews[10,11] and has been shown to affect considerably the *MWD* of the polymer formed.

In the polycondensation of BHET, catalysts are always used[9,12]. Among the various catalysts in use, the most popular is zinc acetate which has been studied by Tomita[9]. In this study they find the average chain length of the polymer to increase at first, subsequently reducing after attaining a maximum. This maximum was explained through the occurrence of a degradation reaction. Instead of evaluating the various rate constants using an exact analysis, Tomita has evaluated two empirical constants. These constants were also found to depend on the rotation speed of the stirrer used. In view of these confusions, we have presented the reactor simulation in
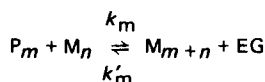

Table 1 Different reactions in PET formation

1. Polycondensation

$$P_m + P_n \underset{k_p'}{\overset{k_p}{\rightleftharpoons}} P_{m+n} + EG$$
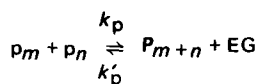
2. Reactions with monofunctional compounds

$$P_m + M_n \underset{k_m'}{\overset{k_m}{\rightleftharpoons}} M_{m+n} + EG$$

3. Redistribution

$$P_m + P_p \overset{k_r}{} P_{m+P-r} + P_r$$

4. Cyclization

(a) $$P_m \underset{nk_c'}{\overset{k_c}{\rightleftharpoons}} C_m + EG$$

(b) $$P_m \underset{nk_c''}{\overset{k_c(n)}{\rightleftharpoons}} C_{m-n} + P_n$$

5. Thermal degradation

$$P_m \overset{k_d}{} Z_r + Z_{m-r}$$

P_n : OH CH$_2$CH$_2$O $-\left[\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}O-CH_2CH_2O\right]_n$ H

M$_1$: CH$_3$(CH$_2$)$_{14}$OH

M$_n$: CH$_3$(CH$_2$)$_{14}$ $-O-\left[\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O\right]_{n-1}$ H

C$_n$: $O-\left[\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}OCH_2CH_2-O\right]_n$

Z$_n$: $\sim\bigcirc-\overset{O}{\overset{\|}{C}}-O$ CH$_2$ CH$_2$

EG : OHCH$_2$CH$_2$OH
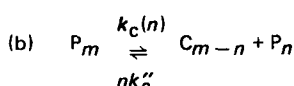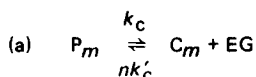
this paper using the rate constants reported by Challa.

The cyclization reaction can occur in two ways as follows:

$$P_m \underset{}{\overset{k_c}{\rightleftharpoons}} C_m + EG \qquad (2)$$

$$P_m \underset{}{\overset{k_c'}{\rightleftharpoons}} C_x + P_{m-x} \qquad (3)$$
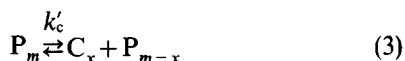
In our earlier work we included only reaction (2). However, Semlyen reports that reaction (3) for cyclization is also important and the equilibrium constant k_c' is chain-length-dependent[1,13]. In this work we have included both these reactions and evaluated the relative importance of reactions (2) and (3) under various polymerization conditions.

There have only been a few simulation studies reported. Ault and Mellichamp[14,15] have simulated the first stage of PET formation in which they included the transesterification and redistribution reactions in addition to the polycondensation step. In this study all

other side reactions were ignored. Ravindranath and Mashelkar[16-19] have recently simulated the first and second stages of PET formation and included etherification, degradation and transesterification with the residual DMT as the side reactions. These studies are, however, limited in scope because they report end group conversion only. They also did not consider the cyclic reaction. We have assumed that the feed consists of BHET alone and therefore there is no transesterification reaction. In view of the importance of the redistribution and cyclic reactions, we have included these in addition to the degradation of polymer. Using the data of Semlyen on the cyclization equilibrium, which is chain-length-dependent, an empirical expression has been derived. We have already pointed out earlier that there is some confusion in the rate constant for the catalysed polycondensation step. As a result, in this work we have used the uncatalysed reaction. We have reported the *MWD* of the polymer formed, the number and weight average molecular weights and the polydispersity index as a function of time, which cannot be obtained through the studies of Mashelkar *et al.*[16-19].

KINETIC MODEL

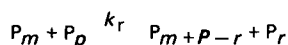The polymerization in the second stage is assumed to have the following side reactions in addition to the polycondensation step:
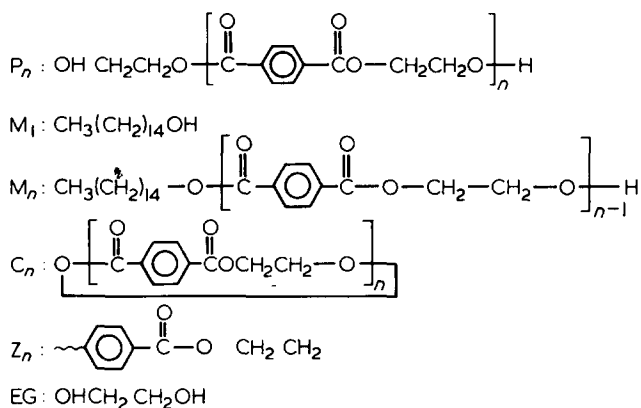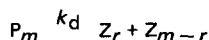
(a) reaction with monofunctional compound (cetyl alcohol),
(b) cyclization reaction with cyclic compounds interacting with ethylene glycol as well as polymer molecules P_n,
(c) redistribution reaction, and
(d) thermal degradation (reaction 5 of *Table 1*).

At any time the reaction mass consists of polymer molecules (P_n), monofunctional compounds (M_n), cyclic compounds (C_n) and degraded polymer chains (Z_n). The mass balance for each of these can now be performed.

Species P_n is *produced* by the following reactions:

(i) P_m ($m < n$) reacts with P_{n-m} by forward reaction or ethylene glycol reacts with $P_{m'}$ ($m' > n$) by reverse reaction in the polycondensation step, i.e.

$$r_1 = 4k_p \times \frac{1}{2} \sum_{m=1}^{n-1} [P_m][P_{n-m}] + 4k_p'[EG] \sum_{m'=n+1}^{\infty} [P_m] \qquad (4)$$

The factor of 4 in the above expression occurs because P_m, P_{m-n} and EG all are bifunctional and can react in four ways.

(ii) Ethylene glycol reacts with M_n, whose chain length is greater than P_n, by the reverse reaction in reaction 2 of *Table 1*, i.e.

$$r_2 = 2k_m'[EG] \sum_{m=n+1}^{\infty} [M_m] \qquad (5)$$

(iii) Two polymer molecules undergo a redistribution reaction to give P_n either as an elimination product or as a combination product, i.e.

$$r_3 = 4k_r \sum_{m=1}^{\infty} [P_m] \sum_{m=n+1}^{\infty} [P_m] + 4k_r \sum_{i=1}^{n-1} \sum_{m=n-i+1}^{n-1} [P_m] \qquad (6)$$

(iv) Cyclic compound (C_n) reacts either with ethylene glycol, by reverse reaction, or with a polymer molecule of chain length less than n, by the reverse reaction, i.e. reaction, i.e.

$$r_4 = +2nk'_c[EG][C_n] + 2\sum_{m=1}^{n-1} mk_{cm}[C_m][P_{n-m}] \quad (7)$$

In this reaction the OH groups in ethylene glycol or polymer react with the reacted bonds of the cyclic compound. So n and m are the number of reacted bonds in the cyclic compounds involved.

Species P_n is *depleted* by the following reactions:
(i) P_n reacts either with polymer or ethylene glycol in the polycondensation step, i.e.

$$r_5 = -4k_p[P_n]\sum_{m=1}^{\infty}[P_m] - 2k'_p[EG](n-1)[P_n] \quad (8)$$

(ii) P_n reacts with M_m by reaction 2 of *Table 1*, i.e.

$$r_6 = -2k_m[P_n]\sum_{m=1}^{\infty}[M_m] \quad (9)$$

(iii) OH of P_n reacts with $(m-1)$ reacted bonds of P_m or its reacted bonds react with OH group of any other polymer species through the redistribution mechanism, i.e.

$$r_7 = -4k_r[P_n]\sum_{m=2}^{\infty}(m-1)[P_m] - 4[P_n]k_r(n-1)\sum_{m=1}^{\infty}[P_m] \quad (10)$$

(iv) P_n either undergoes cyclization reaction or reacts with a cyclic compound, i.e.

$$r_8 = -k_c[P_n] - k_c(n-1)[P_n] - 2[P_n]\sum_{m=2}^{\infty}m[C_m]k''_{cm} \quad (11)$$

The second term appears only for values of $n=3$, since for $n=2$ it turns out to be the same as the first term.

(v) P_n undergoes thermal degradation, i.e.

$$r_9 = -k_d(n-1)[P_n] \quad (12)$$

On adding these, the overall rate of production of P_n is given by

$$\frac{d[P_n]}{dt} = \sum_{i=1}^{9} r_i \quad (13)$$

Similar balance can also be written for all the other species and are given in *Table 2*.

The above-mentioned mass balance equations involve a number of rate constants, some of which are not available in the literature. The activation energies and rate constants of the forward and reverse reactions of polycondensation and that of redistribution reported by Challa have been used in this work. Since the reaction with monofunctional compounds involves the same functional groups as in the polycondensation step, it is reasonable to assume that this reaction has the same reactivity as in the latter, i.e.

$$k_m = k_p \quad (14a)$$

$$k'_m = k'_p \quad (14b)$$

Semlyen reports the equilibrium constant for the cyclization reaction 4(b) of *Table 1* only at one temperature, viz., 270°C. These are found to be chain-length-dependent. To be able to find the equilibrium constant at some other temperature, we assume that for a given chain length n the temperature variation of k is given by the usual thermodynamic relation. Assuming the activation energies for the cyclization reaction to be approximately equal to those for the polycondensation step, the equilibrium constant for various values of n at several temperatures were determined. These k_c values were then curve-fitted at a given temperature by the following relation:

$$1/k_{nT} = A_T\exp(-B_T/n) \quad (15)$$

where A_T and B_T are constants which are independent of chain length n. However, they are functions of temperature and are listed in *Table 3*.

METHOD OF COMPUTATION

A complete set of mass balance equations for the reactions given in *Table 1* are presented in *Table 2*. As seen from the table, it contains a number of rate constants. In order to obtain a numerical solution for the set of differential equations, the rate constants are made dimensionless as follows:

$$R_1 = k'_p/k_p \qquad R_2 = k_m/k'_p$$

$$R_3 = j''/k_p \qquad R_4 = k_c/k_p$$

$$R_5(n) = nk'_c/k_p \qquad R_6 = k_r/k_p \qquad R_7 = R_4 \quad (16)$$

$$R_8(n) = nk''_c/k_p \qquad R_9 = k_d/k_p \qquad x = k_p[P_1]_0 t$$

$$[G] = [EG]/[P_1]_0[MF_1]_0 = [M_1]_0/P_1]_0$$

where $[P_1]_0$ and $[M_1]_0$ are the concentrations of BHET and cetyl alcohol charged to the batch reactors. Using these dimensionless numbers the equations in *Table 2* are solved on a DEC-1090 computer, using the Runge–Kutta method of fourth order. An increment of 0.001 was assumed in x and the integration is carried out up to $x=2.0$. Initially 60 equations were solved and these were later increased by 30 equations at $x=0.5$, 1.0 and 1.5. As seen from the reaction mechanism given in *Table 1*, the benzene ring count should not change. This was therefore used as a means to check the truncation error. In all the computations, the latter was found to be within 1%. Since the presence of cyclic compounds in the polymer creates problems during spinning, they are always extracted out. The molecular weight and the polydispersity index reported in this work have been calculated after excluding the cyclic compounds as follows:

$$W_i = \frac{i[P_n] + i[M_i]}{\sum_{i=1}^{\infty} i([P_i] + [M_i])} \quad (17)$$

Table 2 The balance equations for various species in batch reactors

$$\frac{d[P_n]}{dt} = -4[P_n]k_p \sum_{m=1}^{\infty}[P_m] + 2k_p \sum_{m=1}^{n-1}[P_m][P_{n-m}] + 2k'_p[EG](n-1)[P_n]$$

$$+ 4k'_p[EG]\sum_{m=n+1}^{\infty}[P_m] - 2k_m[P_n]\sum_{m=1}^{\infty}[M_m] + 2k'_m[EG]\sum_{m=n+1}^{\infty}[M_m]$$

$$- k_c[P_n] + 2k'_{cn}[EG][C_n] + k_r\left(-4[P_n]\sum_{m=2}^{\infty}(m-1)[P_m] \right.$$

$$- 4[P_n](n-1)\sum_{m=1}^{\infty}[P_m] + 4\sum_{m=1}^{\infty}[P_m]\sum_{m'=n+1}^{\infty}[P_{m'}]$$

$$\left. + 4\sum_{i=1}^{n-1}\sum_{m=n-i+1}^{\infty}[P_i][P_m] \right) - k_c(n-2)[P_n]$$

$$+ 2\sum_{m=2}^{n-1}m[C_m][P_{n-m}]k''_{cm} - k_d(n-1)[P_n] - 2[P_n]\sum_{m=2}^{\infty}m[C_m]k''_{cm}$$

$$\frac{d[M_n]}{dt} = 2k_m[M_n]\sum_{n=1}^{\infty}[P_n] + 2k_m\sum_{m=1}^{n-1}[M_m][P_{n-m}] - 2k'_m[EG](n-1)[M_n]$$

$$+ 2k'_m[EG]\sum_{m=n+1}^{\infty}[M_m]$$

$$\frac{d[C_n]}{dt} = k_c[P_n] - 2nk'_c[EG][C_n] + 2k_c\sum_{m=n+1}^{\infty}[P_m] - 2nk''_{cm}[C_n]\sum_{m=1}^{\infty}[P_m]$$

$$\frac{d[Z_n]}{dt} = 2k_d\sum_{m=n+1}^{\infty}[P_m]$$

$$\frac{d[P_1]}{dt} = -4[P_1]k_p \sum_{m=1}^{\infty}[P_m] + 4k'_p[EG]\sum_{m=n+1}^{\infty}[P_m] - 2k_m[P_1]\sum_{m=1}^{\infty}[M_m]$$

$$+ 2k'_m[EG]\sum_{m=n+1}^{\infty}[M_m] + k_r\left(-4[P_1]\sum_{m=2}^{\infty}(m-1)[P_m] \right.$$

$$\left. + 4\sum_{m=1}^{\infty}[P_m]\sum_{m=n+1}^{\infty}[P_m] \right) + 2k_c\sum_{m=2}^{\infty}m[C_m]k''_{cm}$$

Table 3 Various rate parameters used in the simulation

Temperature (°C)	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	A_T	B_T
282	2.631*	1.0	2.631	0.01	$R_5 = R_8(n)$	4.78*	0.01	$R_8(N) = (R_4/n)\exp(A_T/n)(-B_T/n)$	0.4104×10^{-4}	2440.6	14.0
300	2.55	1.0	2.55	0.01		5.76	0.01		0.000 054	2321.572	13.75
320	2.63	1.0	2.63	0.01		7.51	0.01		0.000 103	2208.348	12.5
340	2.70	1.0	2.70	0.01		9.64	0.01		0.000 159	2100.646	11.1
360	2.77	1.0	2.77	0.01		12.20	0.01		0.000 214	1998.196	10.6

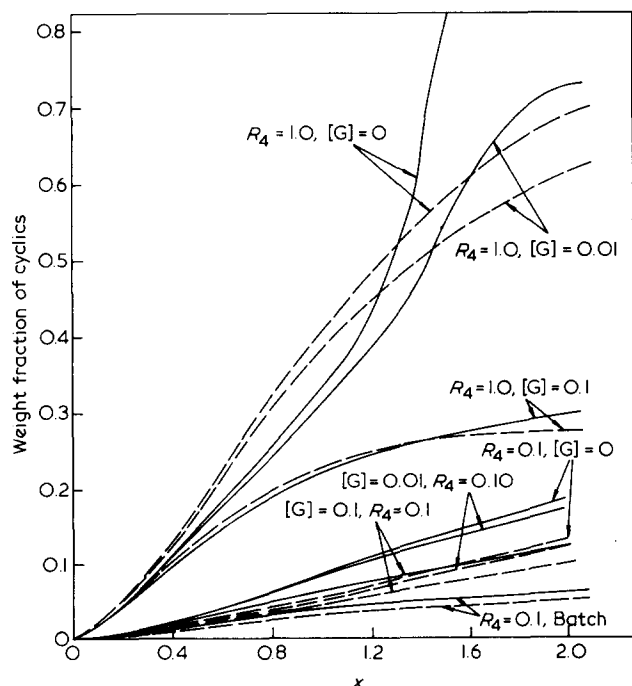* Experimental value taken from refs.2—4

Figure 1 Effect of vacuum and parameter R_4 on the total amount of cyclic formed in the reaction mass. The dotted line is the result for the case when reaction 4(a) of *Table 1* alone is considered. $R_1 = R_3 = 2.631$; $R_2 = 1.0$; $R_6 = 4.781$; $R_9 = 0.4104 \times 10^{-4}$; $[MF_1]_0 = 0.01$

RESULTS AND DISCUSSION

Studies of Ravindranath et al.[16-19] have shown that the overall reaction becomes mass-transfer-controlled only after the mean degree of polymerization, $\overline{DP}$, of the polymer formed increases beyond the value of 30. This would mean that the conversion of functional groups be taken to be 97%. In none of our studies does the conversion reach beyond 90%, which means that the PET reactor of the second stage has been operated in the reaction-controlled region. On application of a vacuum in the reactor, therefore, there is a negligible mass transfer resistance to the removal of the condensation product, ethylene glycol. If there is a concentration profile of ethylene glycol at all in the reaction mass, it is expected to be small, and the reaction mass as a whole could be assumed at some uniform concentration. This concentration can be obtained by the vapour–liquid equilibrium existing at the level of the vacuum applied. In this study we have taken the ethylene glycol concentration as a parameter instead of the pressure applied.

The forward rate constant k_c associated with the cyclization reaction is of first order and it has been shown

to be related to a second-order rate constant k_p and 'mutual concentration' of chain ends of the same molecule given by[20,21]

$$k_c = k_p(\tfrac{3}{2}\langle r^2 \rangle)^{3/2}/N_{av} \qquad (18)$$

where $\langle r^2 \rangle^{\frac{1}{2}}$ is the radius of gyration of the polymer molecule undergoing the cyclization reaction and N_{av} is the Avogadro number. Since the polymer chains are growing in size with the progress of polymerization, k_c is expected to change. In the absence of any information on the nature of this change, $R_4 = k_c/k_p$ has been treated as some average parameter in this study. It has been chosen such that the fraction of cyclic compounds formed in the reaction mass does not increase beyond 5%[20].

In *Figure 1* R_4 has been varied with various uniform ethylene glycol concentrations as a parameter and the fractional weight of the cyclic compounds has been plotted as a function of the dimensionless time x. On the same graph results from our earlier studies[3-5] have also been given in which we had assumed that only reaction 4(a) of *Table 1* occurs. For a given R_4 and vacuum level, the amount of cyclic compounds formed with reaction 4(a) as well as 4(b) of *Table 1* is found to be considerably higher compared to when only reaction 4(a) occurs. As the vacuum is increased, [G] in the reaction mass is lowered and the fraction of cyclic compounds formed is increased and is highest for irreversible polymerization. Having lower values of [G] would push the reaction more in the forward direction, thus giving higher conversion for the same time of reaction. As seen from reactions 4(a) and (b) of *Table 1*, a larger concentration of polymer in the reaction mass would give a larger fraction of cyclic compounds as observed in the figure. The difference between curves calculated in this work (full lines) and earlier (dotted lines) can be attributed to the additional reaction 4(b) of *Table 1* and the results show that it cannot be neglected. For $R_4 = 0.01$ in this study we found that the fraction of cyclic compounds at $x = 2.0$ was within the 5% limit, and therefore this value of R_4 was used in subsequent computational runs. In contrast to this when we assumed the cyclization reaction to occur only through reaction 4(a) of *Table 1* in our earlier studies, we found $R_4 = 0.1$ to give 5% cyclic compound formation. The study in this paper clearly shows the need to obtain k_c more reliably.

In *Figure 2* we have examined the effect of the variation of the redistribution rate constant R_6 on the molecular weight distribution of the polymer obtained from the reactor. When ethylene glycol is not removed from the reaction mass, we find there is no maximum in the weight fraction distribution and R_6 is found to have no effect on it. As the vacuum is increased, different curves are obtained for various values of R_6. The difference between
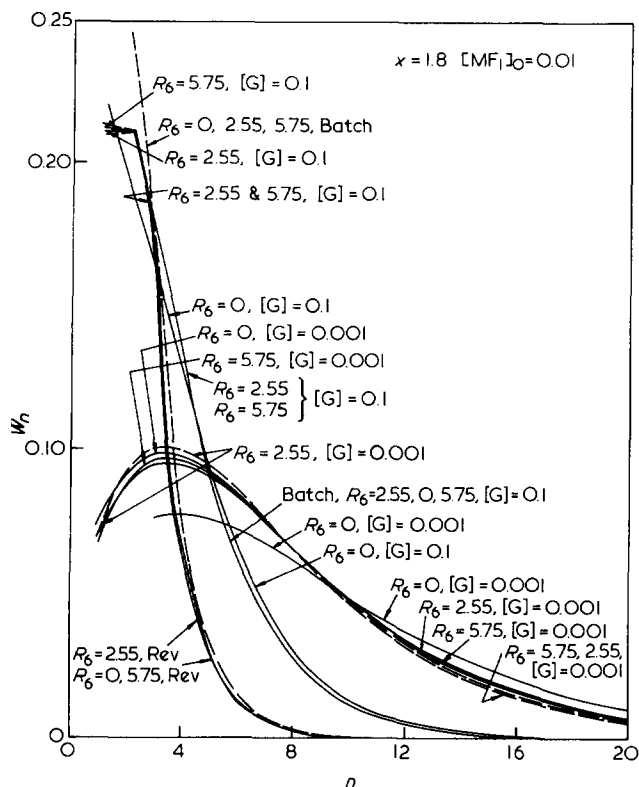
Figure 2 Effect of R_6 and vacuum on the weight fraction distribution of the polymer formed at x = 1.8; $[MF_1]_0$ = 0.1; $R_1 = R_3$ = 2.631; R_2 = 1.0; R_4 = 0.1; R_9 = 0.4104 x 10⁻⁴

these curves increases as the vacuum level is increased and is largest for irreversible polymerization (i.e. [G] = 0). We find that the weight fraction distribution for the latter case (for the same [G] level) is sharper. The effect of the redistribution reaction is to lower the polydispersity index of the polymer formed and would become important as more and more polymer is formed. This would show up as a reduced breadth of the distribution in *Figure 2*. When ethylene glycol is not removed from the reaction mass (results for this case are marked 'Batch' in *Figure 2*), the conversion is small and there is not sufficient polymer to undergo this reaction. As [G] is lowered and polymer is formed, the contribution of this reaction increases. These results have also been compared with those for R_4 = 0.1 and cyclization occurring only through reaction 4(a) of *Table 1*, and the effect of R_6 is found to be much larger in the former case.

In *Figure 3* we have plotted the total amount of degraded polymer as a function of vacuum upon it and have examined the effect of the vacuum. The case where no ethylene glycol is removed from the reaction mass has been denoted by $[G]_{batch}$ on the diagram and it was found that the amount of polymer degraded increases as the vacuum level is increased. It was found to be largest for irreversible polymerization (denoted by [G] = 0 on the diagram). This result is not surprising because in polymerization with no removal of [G] the amount of polymer formed is small and consequently the amount degraded is small. As the vacuum is applied, the total polymer formed for a given time increases, consequently increasing the amount degraded.

In *Figure 4* the effect of vacuum on the *MWD* of the polymer has been examined. The curve marked 'Batch' indicates the case where ethylene glycol is not removed

from the reaction mass and for this case the *MWD* does not undergo a maximu. This is because the conversion of functional groups is small. As the vacuum is applied, the overall polymerization is driven in the forward direction and a larger conversion is obtained for a given time of reaction, and as found in *Figure 5* the *MWD* curves just begin to have a maximum at [G] = 0.1. On comparison with the results of earlier work (i.e. R_4 = 0.1 and
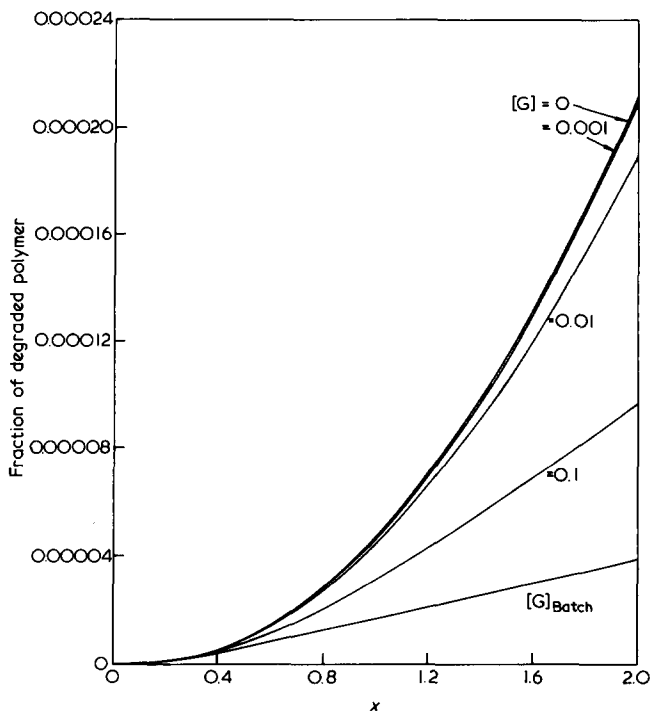

Figure 3 Effect of vacuum on the total amount degraded. $R_1 = R_3$ = 2.631; R_2 = 1.0; R_4 = 0.01; R_6 = 4.781; R_9 = 0.4104 x 10⁻⁴; $[MF_1]_0$ = 0.01
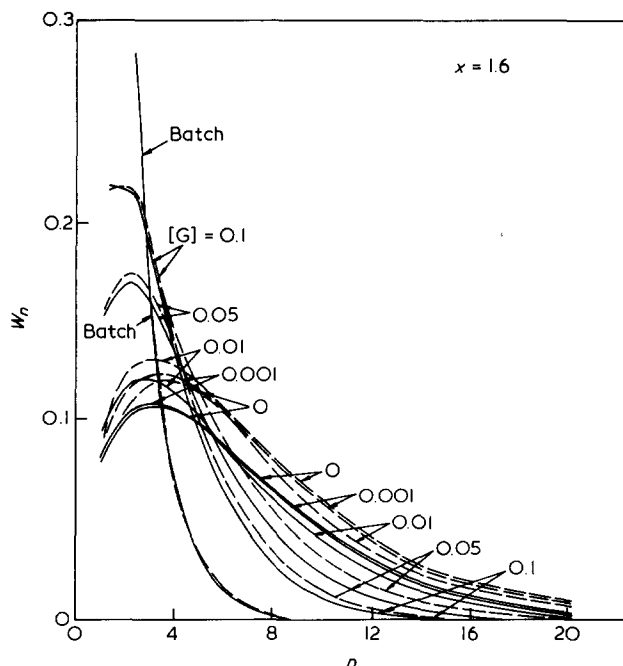

Figure 4 The effect of vacuum on weight fraction distribution. $R_1 = R_3$ = 2.631; R_2 = 1.0; R_6 = 4.781; R_9 = 0.4104 x 10⁻⁴; $[MF_1]_0$ = 0.01
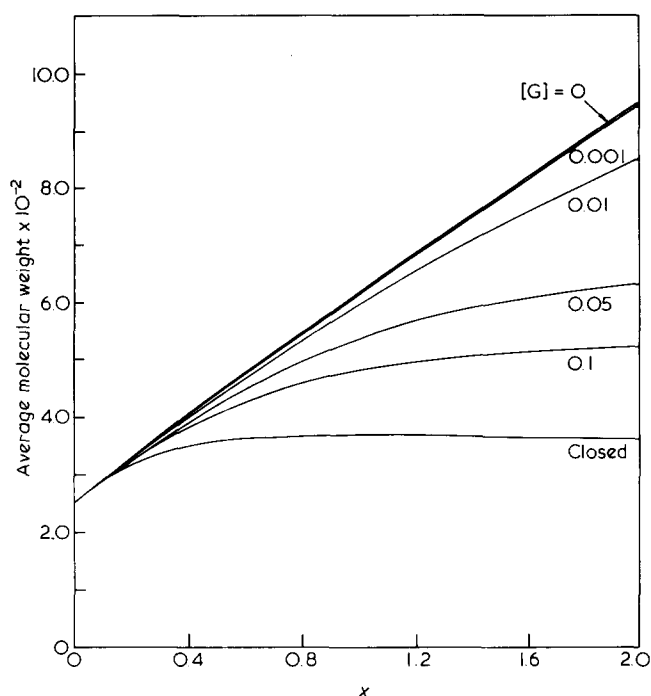
Figure 5 Number average molecular weight versus x for various vacuum levels. $[MF_1]_0 = 0.01$; $R_1 = R_3 = 2.631$; $R_2 = 1.0$; $R_4 = 0.01$; $R_6 = 4.781$; $R_9 = 0.4104 \times 10^{-4}$
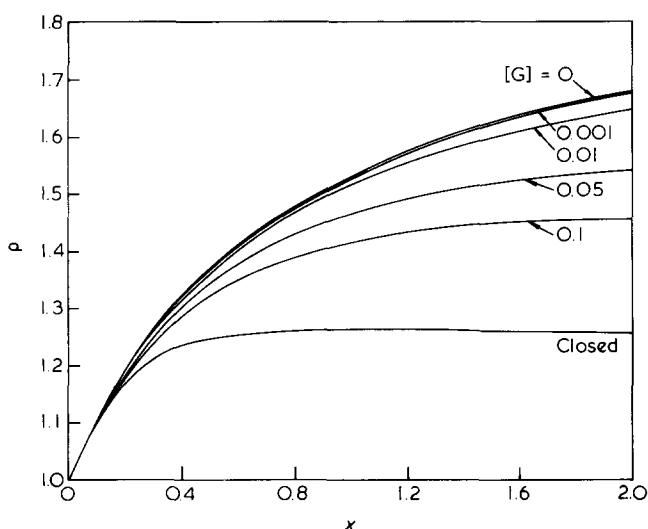

Figure 6 Effect of vacuum on the polydispersity index as a function of x. $[MF_1]_0 = 0.01$; $R_1 = R_3 = 2.631$; $R_2 = 1.0$; $R_4 = 0.01$; $R_6 = 4.781$; $R_9 = 0.4104 \times 10^{-4}$

cyclization to occur only through reaction 4(a) of *Table 1*), we find that the present *MWD* curves are broader for the same vacuum level.

In *Figures 5* and *6* the chain length average and polydispersity index of the polymer formed have been shown as functions of the dimensionless residence time x. Curves marked 'Batch' indicate the polymerization where the condensation product has not been removed and they are found to rise from a small value, reaching an asymptotic level. This asymptotic level increases as the vacuum is increased and is highest for irreversible polymerization.

In *Figure 7* the effect of monofunctional compound in

the feed on the polydispersity index of the polymer formed has been examined. For polymerization with no removal of ethylene glycol, ρ is affected negligibly by the variation of $[MF_1]_0$. However, as the vacuum is increased, its effect on the ρ value is increased even though it remains small.

In *Figures 8* and *9* the effect of temperature and vacuum level on the total degraded polymer and the cyclic compounds formed have been examined. In both these figures, increasing the temperature of polymerization as well as the vacuum level give larger fraction of degraded polymer and total cyclic compounds formed in the reaction mass. This is expected because the corresponding rates of their formations are increased.
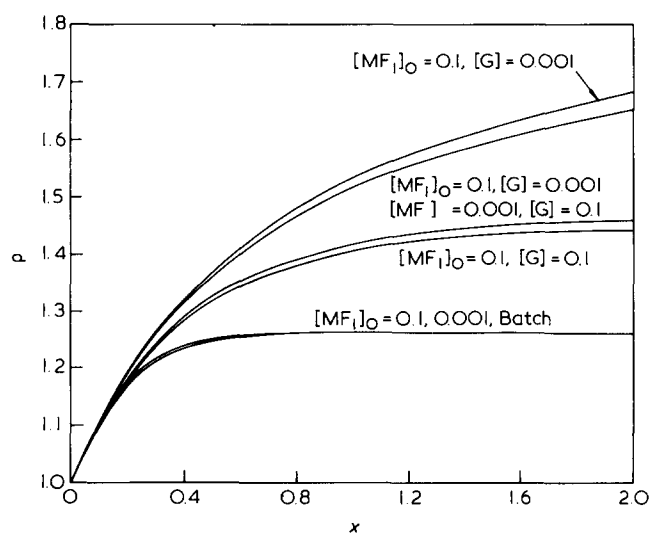

Figure 7 Effect of monofunctional compounds in feed on ρ versus x. $R_1 = R_3 = 2.631$; $R_2 = 1.0$; $R_4 = 0.01$; $R_6 = 4.781$; $R_9 = 0.4104 \times 10^{-4}$
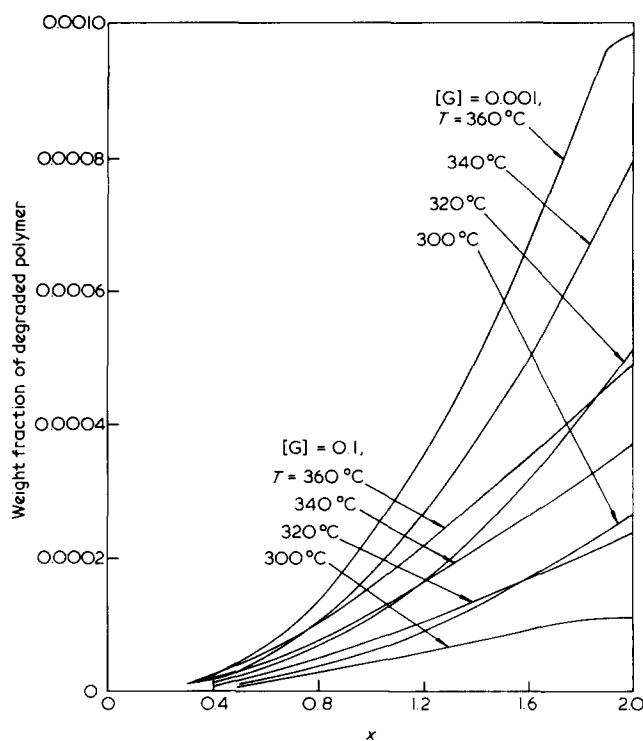

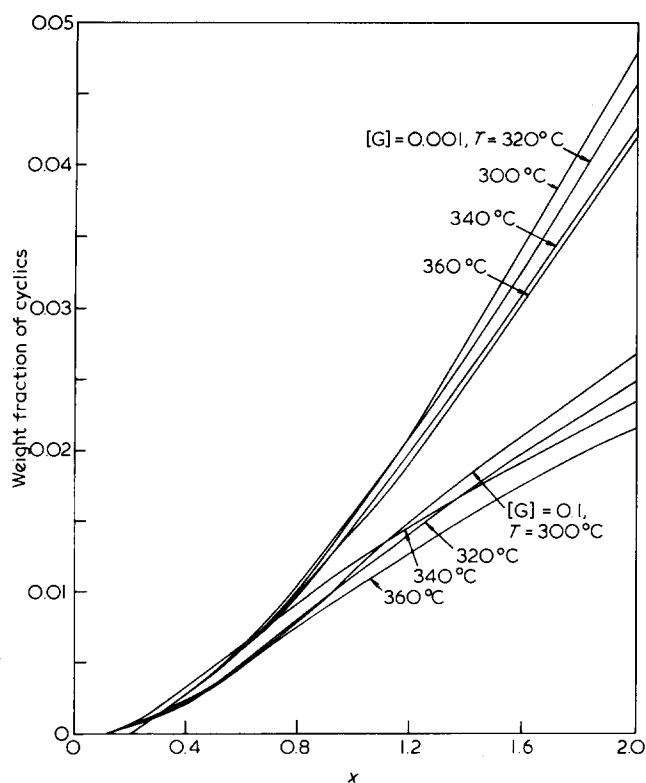*Figure 8* Effect of temperature on amount degraded

Figure 9 Effect of temperature on the amount cyclized

CONCLUSIONS

The second stage of the polyethylene terephthalate reactor has been simulated and side reactions like cyclization, redistribution, reaction with monofunctional compounds and degradation have been included. Even though they are formed in small proportions, they are found to affect the molecular weight distribution of the polymer formed.

Since the equilibrium constant of the polycondensation step is large, it is extremely important that the reaction product, ethylene glycol, be removed from the reaction mass so that the polymerization is driven more in the forward direction. Since the overall polymerization does not become mass-transfer-controlled till about 95% conversion of functional group, the mass transfer resistance to the removal of ethylene glycol could be ignored. The entire reaction mass can thus be assumed to be at some uniform concentration of ethylene glycol given by the vapour–liquid equilibrium, and this has been

treated as a parameter in this study.

The reverse reaction of cyclization can occur either with ethylene glycol or with polymer molecules. The equilibrium constant for the latter is found to depend upon the chain length of the cyclic compound involved and has been reported by Semlyen. These have been curve-fitted into an equation and used in this simulation. Our earlier belief that the contribution to the formation of cyclic compound by reaction 4(b) is small is not correct and both must be considered in my realistic study of PET reactor simulation.

The vacuum applied to the reaction mass appears to be the most important variable. The formation of degraded polymer as well as the amount of cyclic compound formed are increased considerably on reducing [G] in the reaction mass. The effect of temperature and the monofunctional compound $[MF_1]_0$ used in the feed at a given [G] level have been found to have relatively small effect.

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